UNIVERSITY OF PENNSYLVANIA

WEAK ELECTROLYTE EQUILIBRIA IN POTASSIUM CHLORIDE SOLUTIONS

ELWYN FRANCIS CHASE

A THESIS

IN PHYSICAL CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

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This investigation was carried out under the direction of Dr. Martin Kilpatrick, Jr., whom I wish to thank most sincerely for the unfailing patience with which he corrected my blunders and for the generous assistance which he gave throughout the work. I also wish to express my appreciation to Dr. Mary L. Kilpatrick for many helpful suggestions.

DEDICATION

To my wife, without whose assistance this work would have been impossible.

PART 1

THE ELECTROMETRIC AND CATALYTIC DETERMINATION OF HYDROGEN-ION CONCENTRATION. THE MEAN ACTIVITY COEFFICIENTS OF THE IONS OF BENZOIC ACID IN POTASSIUM CHLORIDE SOLUTIONS.

PART 2

THE CLASSICAL DISSOCIATION CONSTANT OF BENZOIC ACID AND THE ACTIVITY COEFFICIENT OF MOLECULAR BENZOIC ACID IN POTASSIUM CHLORIDE SOLUTIONS.

PART 3

THE CLASSICAL DISSOCIATION CONSTANT OF BROMCRESOL GREEN, CHLORPHENOL RED AND METHYL RED IN POTASSIUM CHLORIDE SOLUTIONS.

[Reprint from the Journal of the American Chemical Society, 53, 1732 (1931).]

[Contribution from the Laboratory of Physical Chemistry of the University of Pennsylvania]

THE ELECTROMETRIC AND CATALYTIC DETERMINATION OF HYDROGEN-ION CONCENTRATION. THE MEAN ACTIVITY COEFFICIENTS OF THE IONS OF BENZOIC ACID IN POTASSIUM CHLORIDE SOLUTIONS[1]

By Martin Kilpatrick, Jr., and Elwyn F. Chase[1a]

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In connection with some work on the dissociation constants of indicators in aqueous salt solutions it became necessary to have buffer solutions of known hydrogen-ion concentration. Most buffer systems are standardized in terms of hydrogen-ion activity, the determination being based on certain non-thermodynamic assumptions regarding diffusion potentials. Where the classical dissociation constant is known in a given salt solution, the hydrogen-ion concentration can be calculated. However, accurate values of the dissociation constants are known for few acids except in very dilute solutions. The purpose of the present work is to determine the hydrogen-ion concentration of a series of benzoate–benzoic acid buffers in aqueous solutions of potassium chloride by two different methods. At the same time the mean activity coefficient $\sqrt{f_{H^+} f_{B^-}}$ will be obtained. The method of determining $f_{H^+} f_{B^-}$ the product of the activity coefficients, is as follows. The thermodynamic dissociation constant is equal to

[1] Paper Presented at the Indianapolis Meeting of the American Chemical Society, April, 1931.

[1a] Abstracted in part from the thesis of Elwyn F. Chase to be presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

$$Ka = \frac{a_{H^+}\, a_{B^-}}{a_{HB}} = \frac{C_{H^+}\, C_{B^-}}{a_{HB}}\, f_{H^+}\, f_{B^-}$$

If at constant temperature the solutions are always saturated in respect to benzoic acid, the activity of the molecular benzoic acid is constant in all solutions and its value can be obtained from the solubility in pure water taking into account only that part of the benzoic acid which is present as molecules. At 25° the ionic strength of the saturated benzoic acid solution is approximately 0.001 and the activity of the molecular benzoic acid can be set equal to its concentration within the limits of the error of measurement. The hydrogen-ion concentration is determined by the electrometric and catalytic methods, and the benzoate concentration is calculated from the stoichiometric composition of the buffer. The dissociation constant at zero electrolyte concentration can be determined from conductivity measurements. From these data we calculate the product $f_{H^+}\, f_{B^-}$.

The Electrometric Method

The method employed is the same as that used by Güntelberg and Schiödt[2] and is based on the principle of Brönsted[3] which has been so useful in kinetic problems: "If a salt solution acts as a solvent for other salts, present in concentrations small compared with that of the solvent salt, the variation in the solute system keeping the medium or solvent salt unchanged will not, as in the case of pure water solutions, invalidate the ordinary gas laws and make the mass action law inapplicable." In other words, the activity coefficients of the substances present in small amount are independent of the small quantities of these substances and are determined solely by the salt present in large amount. Thus if we have a set of solutions of low hydrogen-ion concentration in potassium chloride solutions of relatively high concentration, we can assume that the activity coefficient of the hydrogen ion in these solutions of high constant potassium chloride concentration is constant. The assumption of practically complete ionization of the hydrochloric acid gives us a set of standards of known hydrogen-ion concentration. If the hydrogen-ion concentration in the above solutions is 0.01 molar, we do not have to take into account the possible alkalinity of the potassium chloride, which can be kept under 1×10^{-4} M. These standards at various potassium chloride concentrations from 0.01 to 3.0 M were compared with the benzoate–benzoic acid buffers by means of the quinhydrone electrode. The activity coefficient of the hydrogen ion was kept the same in both the standard and the unknown by keeping the ionic strength the same in each, where potassium chloride contributed from 90 to 99% of the ionic strength in practically all cases. The cell measured was

$$\mathrm{Pt} \,\Big|\, Q \,\Big|\, \begin{matrix} c\ \mathrm{HCl}\ \text{and} \\ (m-c)\ \mathrm{KCl} \end{matrix} \,\Big|\, \begin{matrix} \text{Satd.} \\ \mathrm{KCl} \end{matrix} \,\Big|\, \begin{matrix} (m-b)\ \mathrm{KCl}\ \text{and} \\ b\ \mathrm{NaOOCC_6H_5}\ \text{satd. with}\ \mathrm{C_6H_5COOH} \end{matrix} \,\Big|\, Q \,\Big|\, \mathrm{Pt}$$

[2] Güntelberg and Schiödt, *Z. physik. Chem.*, **135**, 393 (1928).

[3] Brönsted, *Trans. Faraday Soc.*, **23**, 430 (1927).

Under the conditions of the experiment the diffusion potential would be small.

Experimental Part

The buffers were prepared by adding potassium chloride and carbonate-free sodium hydroxide solutions to pure benzoic acid in glass bottles and rotating the mixture in a thermostat at 25.15 ± 0.01° until saturated with benzoic acid. It was found that Kahlbaum benzoic acid could be used without further purification. The acid was rotated in the bath for twenty-four hours, a sample of the saturated solution was removed and the acid concentration determined by titration with sodium hydroxide in an atmosphere free from carbon dioxide, using phenol red as indicator. The residue of benzoic acid was then rotated with more water and the solubility redetermined. This was repeated several times and in all cases the determinations agreed within 0.5%. To be certain that twenty-four hours of rotation was sufficient, determinations were made on samples rotated for varying lengths of time up to two hundred hours, without an appreciable change in solubility. Table I summarizes the results of these determinations and Table II gives the values obtained by other workers.

TABLE I

SOLUBILITY OF BENZOIC ACID IN WATER AT 25.15°

Sample	Hours rotated	C_6H_5COOH, moles per liter	Remarks
1	..	0.02773	
2	..	.02776	
3	24	.02783	Fresh sample
3	24	.02773	Fresh sample
4	96	.02781	Fresh sample
4	96	.02778	Fresh sample
5	166	.02780	Fresh sample
5	166	.02780	Fresh sample
6	217	.02784	Residue from 4
6	217	.02788	Residue from 4
7	72	.02778	Residue from 3
7	72	.02782	Residue from 3
8	71	.02790	Twice extracted residue
8	71	.02783	Twice extracted residue
	Av.	.02781	

TABLE II

SOME PREVIOUS DETERMINATIONS OF THE SOLUBILITY OF BENZOIC ACID IN WATER AT 25°

Solubility, moles per liter	Observer
0.028082	Paul, *Z. physik. Chem.*, **14**, 105 (1894).
.02793	Noyes and Chapin, THIS JOURNAL, **20**, 751 (1898).
.02796	Hoffmann and Langbeck, *Z. physik. Chem.*, **51**, 385 (1905).
.02799	Freundlich and Seal, *Kolloid Z.*, **11**, 257 (1912).
.02791	Rørdam, *Thesis, University of Copenhagen*, **1925**.
.02781	Larsson, *Z. anorg. Chem.*, **155**, 247 (1926).

The potassium chloride was Kahlbaum "with certificate of guarantee" and the small quantities of alkali present could be neglected in the well-buffered solutions. The standard hydrochloric acid solutions were prepared from weighed amounts of potassium chloride and constant boiling hydrochloric acid made according to Hulett.

The cell as shown in Fig. 1 consisted of two cylindrical electrode vessels A and A′ of Pyrex glass connected through stopcocks B and B′ to the reservoir C for the saturated potassium chloride solution. The electrodes D and D′ were pieces of bright platinum foil which were cleaned and heated to redness just before using. Constrictions at E and E′ served to hold cotton plugs on which the quinhydrone was placed. Through the inlets F and F′ nitrogen was passed into the solution to remove dissolved oxygen and to keep the solutions stirred, while the tubes G and G′ served for adjusting the junctions H and H′ and for emptying the vessels. The apparatus was set in a thermostat at 25.15 ± 0.05°.

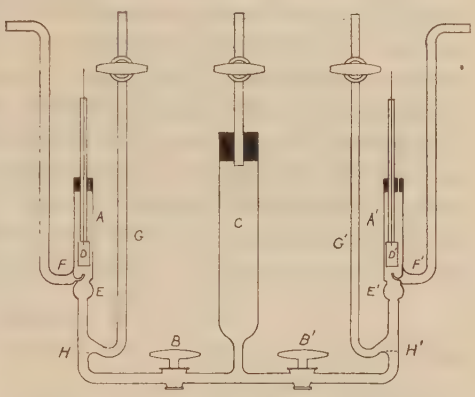


Fig. 1.—The quinhydrone cell.

The method of carrying out a determination was as follows. The standard hydrochloric acid solution in potassium chloride and the buffer solution were placed in A and A′, respectively, and carbon dioxide-free nitrogen was bubbled through the solutions. By gentle suction at G and G′ the junctions were made at H and H′. Quinhydrone was added from a spatula and the electrodes were set in place. The potential difference was measured by means of a Type K Leeds and Northrup potentiometer and a suitable galvanometer. The readings were usually constant to 0.0001 volt for the first fifteen minutes. Over the range studied 0.0001 volt represents approximately 0.3% in hydrogen-ion concentration. In general the results were reproducible to 1% in hydrogen-ion concentration.

The cell reaction is

$$\text{Quinhydrone} + 2H^+ + 2e \longrightarrow \text{Hydroquinone}$$

and the potential is given by

$$E = E_0 + \frac{RT}{2F} \ln \frac{a_{Hy}}{a_Q a_H^2} = E - \frac{RT}{F} \ln a_H + \frac{RT}{2} \ln \frac{f_{Hy}}{f_Q}$$

since $C_{Hy} = C_Q$. The last term is the salt error which cancels out in our experiments because the activity coefficients in both solutions are equal. Since at constant potassium chloride concentration we may replace the

ratio of the activities of the hydrogen ion by the ratio of the concentrations and

$$\Delta E = \frac{RT}{F} \ln \frac{C'_{H^+}}{C_{H^+}} = 0.05914 \log \frac{C'_{H^+}}{C_{H^+}}$$

and

$$\log C'_H = \frac{\Delta E}{0.05914} + \log C_{H^+}$$

where C_{H^+} is the known concentration of the hydrogen ion in the standard solution of hydrochloric acid in potassium chloride and C'_{H^+} is the hydrogen-ion concentration of the buffer solution.

Table III gives the results of these determinations. The concentration of potassium chloride in each standard solution can be obtained by subtracting the hydrogen-ion concentration as given in Column 2 from the total electrolyte concentration as given in Column 1. Similarly the difference between Column 1 and the concentration of the sodium ion in Column 5 gives the concentration of potassium chloride for the buffer solutions.

TABLE III

THE ELECTROMETRIC DETERMINATION OF THE HYDROGEN-ION CONCENTRATION (25.15°)

Standard solution			Buffer				
Electrolyte KCl + HCl, moles per liter	H_3O^+, moles per liter $\times 10^5$	E. m. f., volts	H_3O^+, moles per liter $\times 10^5$	Na^+, moles per liter $\times 10^5$	$C_6H_5COO^-$, moles per liter $\times 10^5$	C_{H^+} $\times 10^7$	C_{B^-}	Av.
0.1000	1035	0.07859	48.5	480.9	529.4	25.6		
.1000	1035	.08869	32.8	734.5	767.3	25.6		
.1000	1035	.09553	25.1	1000	1025	25.8		
.1000	1035	.11188	13.3	1852	1865	24.9		
.1000	1035	.11187	13.3	1852	1865	24.9		25.5
.2000	933.1	.08479	34.3	727.3	761.6	26.1		
.2000	933.1	.10452	15.9	1647	1660	26.4		
.2000	933.1	.12289	7.79	3293	3301	25.7		26.1
.3000	878.5	.10343	15.6	1647	1663	25.9		
.3000	878.5	.10395	15.0	1729	1744	26.1		
.3000	878.5	.11364	10.5	2470	2481	26.0		
.3000	878.5	.12082	7.94	3293	3301	26.2		26.1
.4000	1050	.10811	15.6	1647	1663	25.9		
.4000	1050	.10911	15.0	1729	1744	26.1		
.4000	1050	.11888	10.2	2470	2480	25.3		
.4000	1050	.12581	7.82	3293	3302	25.8		25.8
.5000	1002	.06490	80.1	240.4	320.5	25.6		
.5000	1002	.11183	12.9	1976	1989	25.8		
.5000	1002	.13265	5.72	4323	4329	24.8		
.5000	1002	.13241	5.78	4323	4329	25.0		25.3
.6000	999.3	.10779	15.0	1647	1662	24.9		
.6000	999.3	.10905	14.3	1729	1743	24.9		
.6000	999.3	.11818	10.0	2470	2480	24.8		
.6000	999.3	.11837	9.94	2470	2480	24.6		24.8

TABLE III (*Concluded*)

Standard solution			Buffer				
Electrolyte KCl + HCl, moles per liter	H_3O^+, moles per liter $\times 10^5$	E. m. f., volts	H_3O^+, moles per liter $\times 10^5$	Na^+, moles per liter $\times 10^5$	$C_6H_5COO^-$, moles per liter $\times 10^5$	$C_{H^+} C_{B^-}$ $\times 10^7$	Av.
0.7000	1014	0.10944	14.3	1647	1661	23.7	
.7000	1014	.11953	9.64	2470	2480	23.9	
.7000	1014	.12742	7.09	3293	3300	23.4	
.7000	1014	.12761	7.04	3293	3300	23.2	23.6
.9000	1016	.11087	13.5	1647	1661	22.4	
.9000	1016	.12169	8.88	2470	2479	22.0	
.9000	1016	.12187	8.84	2470	2479	21.9	
.9000	1016	.12932	6.60	3293	3300	21.8	
.9000	1016	.12936	6.58	3293	3300	21.7	22.0
1.012	961.0	.09446	24.3	850	874.3	21.2	
1.012	961.0	.10551	15.8	1318	1334	21.1	
1.012	961.0	.11090	12.8	1647	1660	21.2	
1.012	961.0	.11606	10.5	1976	1987	20.8	
1.012	961.0	.13045	5.97	3293	3299	19.7	
1.012	961.0	.12885	6.36	3330	3336	21.2	
1.012	1067	.13950	4.66	4323	4328	20.2	
1.012	961.0	.13988	4.14	5000	5004	20.8	20.8
1.500	972.0	.07336	55.8	240.4	296.2	16.5	
1.500	972.0	.12026	8.98	1852	1861	16.7	
1.500	972.0	.12270	8.17	1976	1984	16.2	
1.500	972.0	.14387	3.58	4323	4327	15.5	
1.500	972.0	.14323	3.67	4323	4327	15.9	16.2
2.000	1122	.10201	18.3	617.5	635.8	11.6	
2.000	1122	.12106	10.1	1235	1245	12.6	
2.000	1122	.13213	6.53	1852	1859	12.1	
2.000	1122	.15408	2.78	4298	4301	12.0	
2.000	1122	.15380	2.81	4298	4301	12.1	12.1
2.500	996.5	.10815	14.8	617.5	632.3	9.35	
2.500	996.5	.12580	7.42	1235	1242	9.23	
2.500	996.5	.13884	4.47	1976	1980	8.86	
2.500	996.5	.13897	4.45	1976	1980	8.81	
2.500	996.5	.13842	4.54	1976	1981	8.99	9.05
3.000	1040	.11659	11.1	586.0	597.1	6.64	
3.000	1040	.12955	6.69	988	995	6.65	
3.000	966.1	.12792	6.63	988	995	6.60	6.63

The Catalytic Method

The catalytic method has been used for the determination of hydrogen-ion concentration in a number of cases but as in the case of the electrometric and colorimetric methods a proper consideration of the electrolyte effect is necessary for accurate determinations. In addition, in choosing a suitable reaction we have to consider, as well as the effect of the hydrogen ion, possible catalytic effects of acids other than the hydrogen ion. Both

TABLE IV

THE ELECTROMETRIC DETERMINATION OF THE HYDROGEN-ION CONCENTRATION AT 20°

Standard solution Electrolyte KCl + HCl, moles per liter	H_3O^+, moles per liter $\times 10^5$	E. m. f., volts	Buffer H_3O^+, moles per liter $\times 10^5$	Na^+, moles per liter $\times 10^5$	$C_6H_5COO^-$, moles per liter $\times 10^5$	$C_{H^+} C_{B^-} \times 10^7$	Av.	G. + S. av.
1.000	200	0.0292	62.8	200.0	262.8	16.5		
1.000	500	.06918	32.3	500.0	532.3	17.2	16.9	
2.000	500	.0828	18.7	500.0	518.7	9.81	9.81	
3.000	200	.0538	23.7	200.0	223.7	5.30		
3.000	500	.0977	10.5	500.0	510.5	5.36	5.33	5.16
NaCl								
1.000	200	.0299	61.3	200.0	261.3	16.0		
1.000	500	.0703	30.9	500.0	530.9	16.4	16.2	
2.000	200	.0425	37.1	200.0	237.1	8.43		
2.000	500	.0855	17.0	500.0	517.0	8.79	8.61	
3.000	200	.0600	18.6	200.0	218.6	4.07		
3.000	500	.1078	8.5	500.0	508.5	4.32	4.20	4.18
4.000	200	.0810	8.10	200.0	208.1	1.69		
4.000	500	.1249	3.60	500.0	503.6	1.81	1.76	1.82
5.000	200	.1015	4.57	200.0	203.6	0.733		
5.000	500	.1481	1.40	500.0	501.4	0.702	0.717	0.741

NOTE.—Table IV gives some measurements carried out by Mr. W. H. Berry at 20° which are given for comparison with the results of Güntelberg and Schiödt and to complete the values over the whole concentration range. They are not to be considered as accurate as the measurements of Güntelberg and Schiödt.

of these factors have been discussed in the recent paper of Brönsted and Grove.[4]

Brönsted and Wynne-Jones[5] used the rate of hydrolysis of diethyl acetal to determine the hydrogen-ion concentration of formic acid buffer solutions at ionic strengths up to 0.05. They showed that this reaction was not catalyzed by acids weaker than the hydrogen ion (H_3O^+) and Brönsted has calculated that in all cases the effect of acids stronger than the hydrogen ion (H_3O^+), such as hydrochloric acid, will hardly be detectable in aqueous solution.[6] In order to know the proportionality between the rate of reaction and the hydrogen-ion concentration for a given medium, Brönsted and Wynne-Jones determined the rate of reaction in a solution of hydrochloric acid in potassium nitrate and assumed that the same proportionality factor could be used for formic acid–sodium formate buffer solutions. A similar assumption has been used by previous workers.[7] However, as further studies of primary salt effect have been made for these zero type reactions (a reaction between an ion and a non-electrolyte), it has been

[4] Brönsted and Grove, THIS JOURNAL, **52**, 1394 (1930).

[5] Brönsted and Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

[6] Brönsted, *ibid.*, **24**, 630 (1928).

[7] See Kilpatrick, THIS JOURNAL, **48**, 2091 (1926).

realized that although the effect is linear in conformity with the theory the magnitude of the effect between $\mu = 0.01$ and $\mu = 0.10$ for uni-univalent electrolytes is in many cases much greater than the 2 to 4% stated for the reactions studied previous to 1922.[8] For the decomposition of nitrosotriacetonamine catalyzed by hydroxyl ion, the effect between $\mu = 0.01$ and $\mu = 0.10$ is 7% when sodium chloride is the solvent salt.[7] For the hydration of ethylene oxide catalyzed by hydrogen ion it is 9% for the solvent salt sodium perchlorate over the same range of concentration.[9] In the hydrolysis of diazoacetic ester catalyzed by hydrogen ion it is 14% for the same solvent salt and for the hydrolysis of diethyl acetal it is 11% for potassium chloride and approximately 13% for sodium chloride and potassium nitrate. The last two values are from Brönsted and Wynne-Jones[5] and are doubtful in that the concentration of strong acid used was only 0.0008 *M*. Brönsted and Grove[4] extended these studies to other acetals studied originally by Skrabal[10] and found that the primary salt effect is large and varies with the individual salt to such an extent that one is confined to the determination of the hydrogen-ion concentrations of unbuffered solutions of weak acids where the electrolyte concentration is below $\mu = 0.01$.[11]

Our problem was to determine the hydrogen-ion concentration of the benzoate buffers up to 3.0 molar concentration of potassium chloride. A search of the literature failed to reveal a suitable reaction with a small electrolyte effect, so the hydrolysis of diethyl acetal was used. As already pointed out, the primary salt effect cannot be studied at 25° because we must deal with such low concentrations of strong acids that the results are uncertain. Our method consisted of determining the electrolyte (salt) effect at 0° where the reaction is slow enough to permit the use of 0.01 to 0.005 molar hydrochloric acid. By determining accurately the temperature coefficient, which from previous experience would be expected to be independent of electrolyte concentration,[12,7] the proportionality of the rate to the hydrogen-ion concentration for the various concentrations of solvent salt at 25.15° was calculated. Then by determining the rate of reaction with the benzoate–benzoic acid buffer solutions we obtained the hydrogen-ion concentration.

Experimental Method

The experiments at 0° were carried out in a dilatometer previously used for the determination of the rate of hydration of acetic anhydride.[13] It was

[8] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).
[9] Brönsted, Kilpatrick and Kilpatrick, This Journal, **51**, 420 (1929).
[10] Skrabal, *Z. Electrochem.*, **33**, 322 (1927).
[11] Grove, This Journal, **52**, 1404 (1930).
[12] Rice and Lemkin, *ibid.*, **45**, 1896 (1923).
[13] Kilpatrick, *ibid.*, **50**, 2891 (1928).

found very convenient to have the whole apparatus in a refrigerator room which was kept a few degrees above the freezing point of water. Two samples of acetal were used and gave the same results. Preparation A boiled between 102 and 103° (760 mm.), while preparation B was very carefully fractionated and boiled at 103° (759 mm.). Preparation B was completely free from acidic impurities. Table V gives the results of the experiments in various concentrations of potassium chloride at 0°.

TABLE V

THE ELECTROLYTE EFFECT ($t = 0.0°$)

KCl, moles per liter	HCl, moles per liter	μ, ionic strength	$k_{observed}$	$\frac{k_{obs.}}{C_{HCl}} = k_{H_3O^+}$
0.0	0.01315	0.013	0.0326	2.48[a]
.087	.01315	.10	.0372	2.74
.20	.00933	.21	.02885	3.08
.40	.00933	.41	.0391	3.73[a]
.60	.00395	.60	.0174	4.51[a]
1.0	.01247	1.01	.0742	6.08
1.5	.00395	1.50	.03312	8.38
2.0	.00658	2.01	.0715	10.87
2.0	.00395	2.00	.0445	11.25

[a] = acetal sample B

The salt effect from 0.01 to 0.10 molar is 10% and over the range studied changes from 2.48 to 11.25, a four-fold increase. Experiments at higher

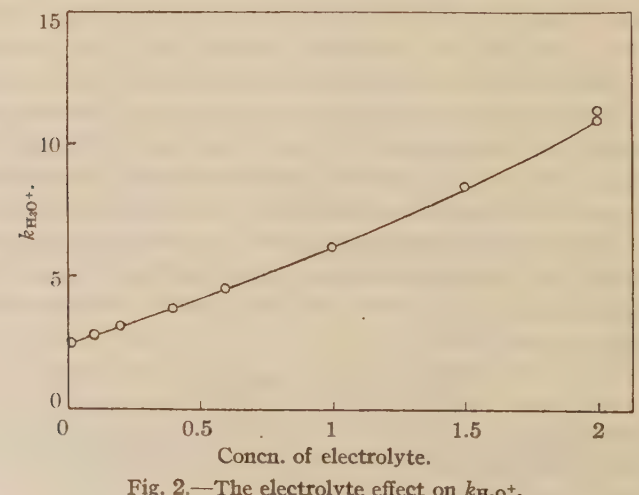


Fig. 2.—The electrolyte effect on $k_{H_3O^+}$.

concentrations of potassium chloride show an even greater effect between 2 and 3 molar but these results are more uncertain than the others, due to the lower hydrochloric acid concentrations, and are not given here. In Fig. 2 $k_{H_3O^+}$ is plotted against the electrolyte concentration. The electrolyte

effect is linear and for dilute solutions the experimental results can be expressed by the equation

$$k = 2.40 + 3.40\,c$$

where c represents the total equivalent electrolyte concentration. To emphasize again the dependence of the effect upon the individual nature of the salt, $k_{H_3O^+}$ for a solution 0.75 M in potassium nitrate is 4.34 as against 5.04 for the corresponding potassium chloride solution.

The temperature coefficient was determined by the two-thermostat method.[14] The reaction was followed dilatometrically, the reacting solutions being confined in two dilatometers similar in design to that used in the study of the hydration of ethylene oxide.[15] The dilatometers were placed in thermostats regulated to $\pm 0.003°$ and at temperatures exactly five degrees apart as determined by a calibrated resistance thermometer. Portions of a solution of suitable acid concentration were placed in the mixing chambers of the dilatometers and after thermal equilibrium was established with the baths, acetal was added. The velocity constants were determined in the usual way. Although the hydrogen-ion concentrations were too small to be known accurately they were the same in both cases and the temperature coefficient was obtained directly from the velocity constants. The results are given in Table VI, which also contains the heat of activation E calculated from the Arrhenius equation.

Table VI

The Temperature Coefficient

KCl, moles per liter	0	0	0	0	1.0	2.0
$k_{25.00}/k_{20.00}$	1.870	1.893	1.887	1.894	1.923	1.944
E, cal. per degree	21,720	22,150	22,000	22,160	22,690	23,070

The temperature coefficient seems to increase slightly with increasing salt concentration but this may be due to experimental error and we have given E an average value of 22,300 calories from which we calculated $k_{25.15}/k_0 = 32.19$. An error of 1% in k_{25}/k_{20} means about the same percentage error in E, which would mean a possible error of 3% in $k_{25.15}/k_0$. The velocity constant $k_{H_3O^+}$ for 25.15° is determined by multiplying $k_{H_3O^+}$ for 0° for each electrolyte concentration by 32.19.

Table VII gives the results of the determinations of hydrogen-ion concentration in the buffer solutions. In Column 6 are given the hydrogen-ion concentrations as determined by the electrometric method.

The agreement between the two methods is fairly good, the catalytic method giving slightly lower values above 1 molar concentration of electrolyte. At higher electrolyte concentrations the deviations obtained are greater, apparently exceeding the experimental error. These differences

[14] Rice and Kilpatrick, This Journal, **45**, 1401 (1923).

[15] Ref. 9, p. 428.

TABLE VII

THE CATALYTIC DETERMINATION OF THE HYDROGEN-ION CONCENTRATION

Total equivalent electrolyte, $KCl + C_6H_5COO^-$, moles per liter	Na^+, moles per liter $\times 10^5$	$k_{observed}$	$k_{H_3O^+}$	$\frac{k_{obs.}}{k_{H_3O^+}} = H_3O^+$, moles per liter $\times 10^5$	E. m. f. method, H_3O^+, moles per liter $\times 10^5$	$C_{H^+} C_{B^-}$ $\times 10^7$
0.0013[a]	0.0	0.1017	77.4	131.6		17.0
.0998	734.5	.02960	88.3	33.6	32.8	25.8
.2000	741.0	.03510	99.2	35.4	35.5	27.4
.3000	1729	.01730	112.7	15.4	15.0	26.8
.4000	1729	.01856	120.1	15.5	15.0	26.9
.5000	1976	.01688	135.2	12.5	12.9	24.9
.6000	1729	.02036	145.2	14.0	14.3	24.4
.8000	1729	.02166	167.8	12.9	13.3	22.5
1.012	3293	.01143	195.7	5.84	5.97	19.3
1.500	1976	.02070	270	7.69	8.17	15.3
2.000	4298	.00993	362	2.74	2.78	11.8

[a] Saturated solution of benzoic acid.

are being considered further in connection with the assumptions upon which both methods are based, in particular the assumption of practically complete ionization of the hydrochloric acid in potassium chloride solutions and the assumption that the reaction is a pure hydrogen-ion catalysis.

TABLE VIII

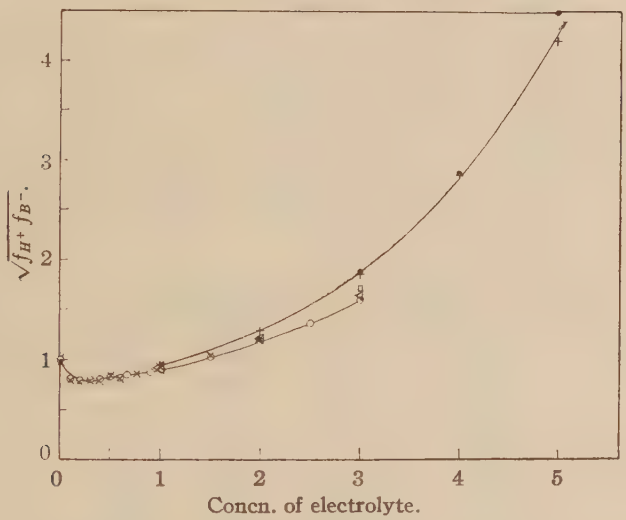
THE MEAN ACTIVITY COEFFICIENT OF THE IONS OF BENZOIC ACID

Total electrolyte concentration $KCl + C_6H_5COONa$	$\sqrt{f_{H^+} f_{B^-}}$ (25°) from e. m. f.	$\sqrt{f_{H^+} f_{B^-}}$ (25°) from catalysis	$\sqrt{f_{H^+} f_{B^-}}$ (20°) from e. m. f., Berry	$\sqrt{f_{H^+} f_{B^-}}$ (20°) G. + S.
0.001	..	0.98		
.1	0.81	$.80_5$		
.2	.80	.78		
.3	.80	.79		
.4	$.80_5$	.79		
.5	.81	.82		
.6	.82	.83		
.7	.84	..		
.8	..	.86		
.9	.87	..		
1.01	.90	.93	0.92	
1.5	1.02	1.04	..	
2.0	1.18	1.19	1.21	
2.5	1.36	..	..	
3.0	1.59	..	1.64	1.70
$NaCl + C_6H_5COONa$				
1.0			0.94	..
2.0			1.29	..
3.0			1.85	1.89
4.0			2.85	2.86
5.0			4.19	4.48

The values of the mean activity coefficients of the ions of benzoic acid can be calculated from the following equation

$$\sqrt{f_{H^+} f_{B^-}} = \sqrt{\frac{Ka\, a_{HB}}{C_{H^+}\, C_{B^-}}}$$

the product $C_{H^+}\, C_{B^-}$ being given in Tables III and VII. Ka is set equal to 6.31×10^{-5}.[16] The value for the activity of the molecular benzoic acid is obtained from the solubility of benzoic acid in water by subtracting the small part present as ions, a_{HB} being set equal to 0.0265. Table VIII gives the values of $\sqrt{f_{H^+} f_{B^-}}$ from the electrometric and catalytic methods at the various concentrations of electrolyte (potassium chloride and benzoate). For comparison we have included the values of Berry and those of Güntelberg and Schiödt in sodium chloride solutions.



⊙, E. m. f., 25°; ×, catalytic, 25°; ◁, Berry, 20°; □, G. + S., 20° (in KCl); +, Berry, 20°; ●, G. + S., 20° (in NaCl); ♂, Simons.

Fig. 3.—Mean activity coefficients of the ions of benzoic acid in KCl and NaCl solutions.

From Table VIII and Fig. 3 it is to be noted that the mean activity coefficient is higher in solutions of sodium chloride than in the corresponding solutions of potassium chloride in all cases. Güntelberg and Schiödt[2] interpret this as being due to the predominance of the "salting out" effect over that of interaction.

In another communication will be given the activity coefficients of the molecular acid determined from solubility measurements and K_c, the

[16] This value has been determined by J. K. Simons by conductance measurements and will be the subject of another communication.

classical dissociation constant. At that time a comparison will be made of the activity coefficients of benzoic acid and those of other acids.

Summary

The hydrogen-ion concentrations of benzoic acid–benzoate buffers saturated with benzoic acid in potassium chloride solutions have been determined by two independent methods.

The results obtained by the catalytic method are in agreement with those determined by the quinhydrone electrode.

In both cases "electrolyte effects" have been considered.

The mean activity coefficients of the ions of benzoic acid have been determined in potassium and sodium chloride solutions.

PHILADELPHIA, PENNSYLVANIA

[Reprint from the Journal of the American Chemical Society, 53, 2589 (1931).]

[Contribution from the Laboratory of Physical Chemistry, University of Pennsylvania]

THE CLASSICAL DISSOCIATION CONSTANT OF BENZOIC ACID AND THE ACTIVITY COEFFICIENT OF MOLECULAR BENZOIC ACID IN POTASSIUM CHLORIDE SOLUTIONS[1,2]

By Elwyn F. Chase and Martin Kilpatrick, Jr.

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In a previous paper[3] the authors reported the hydrogen-ion concentration of a series of benzoic acid–benzoate buffers in aqueous potassium chloride solutions. From these values and the composition of the buffer the product of the concentration of hydrogen and benzoate ions was calculated. In all cases the solutions were saturated with benzoic acid so that a determination of the solubility of the acid in these solutions enables one to calculate the classical dissociation constant and the activity coefficient of the molecular benzoic acid. The solubility of the molecular acid is obtained by subtracting the hydrogen-ion concentration from the total concentration of benzoic acid as determined by titration. Column 3 of Table I gives the solubility of benzoic acid in the various solutions and Column 5 gives the amount present as molecular acid.

Table I

The Solubility of Benzoic Acid in Potassium Chloride Solutions at 25.15°

	Moles per liter				
Electrolyte KCl + NaB	Benzoate $\times 10^5$	Total benzoic acid	$C_{H^+} \times 10^5$	Molecular benzoic acid	Average
0.0013	131.0	0.02781	131.0	0.02650	0.02650
.1000	529.4	.0261	48.5	.0256	
	767.3	.0256	32.8	.0253	
	1025	.0259	25.1	.0256	.0255
.2000	761.6	.0251	34.3	.0248	
	1660	.0250	15.9	.0248	
	3301	.0254	7.79	.0253	.0250
.3000	1663	.0242	15.6	.0240	
	1744	.0241	15.0	.0239	
	2481	.0244	10.5	.0243	
	3301	.0244	7.94	.0243	.0241
.4000	1663	.0235	15.6	.0233	
	1744	.0228	15.0	.0226	
	2480	.0229	10.2	.0228	
	3302	.0236	7.82	.0235	.0231

[1] Abstracted from the thesis of Elwyn F. Chase presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Paper presented before the Indianapolis meeting of the American Chemical Society, March 30–April 3, 1931.

[3] Kilpatrick and Chase, This Journal, 53, 1732 (1931).

TABLE I (*Concluded*)

Electrolyte KCl + NaB	Moles per liter: Benzoate $\times 10^5$	Total benzoic acid	$C_{H^+} \times 10^5$	Molecular benzoic acid	Average
0.5000	320.5	0.0232	80.1	0.0224	
	1989	.0223	12.9	.0222	
	4329	.0231	5.78	.0230	0.0225
.6000	1662	.0220	15.0	.0218	
	1743	.0219	14.3	.0218	
	2480	.0221	10.0	.0220	.0219
.7000	1661	.0213	14.3	.0212	
	2480	.0213	9.64	.0212	
	3300	.0216	7.09	.0215	.0213
.9000	1661	.0199	13.5	.0198	
	2479	.0200	8.88	.0199	
	3300	.0202	6.60	.0201	.0199
1.012	874.3	.0184	24.3	.0182	
	1334	.0192	15.8	.0190	
	1660	.0193	12.8	.0192	
	1987	.0191	10.5	.0190	
	3299	.0191	5.97	.0190	
	3336	.0193	6.36	.0192	
	4328	.0190	4.66	.0190	
	5004	.0194	4.14	.0194	.0190
1.500	296.2	.0169	55.8	.0163	
	1861	.0168	8.98	.0167	
	1984	.0164	8.17	.0163	
	4329	.0170	3.67	.0170	.0166
2.000	635.8	.0135	18.3	.0133	
	1245	.0138	10.1	.0137	
	1859	.0141	6.53	.0140	
	4301	.0139	2.81	.0139	.0137
2.500	632.3	.0120	14.8	.0119	
	1242	.0121	7.42	.0120	
	1980	.0123	4.54	.0123	.0121
3.000	597.1	.0102	11.1	.0101	
	994.7	.0103	6.69	.0102	.0102

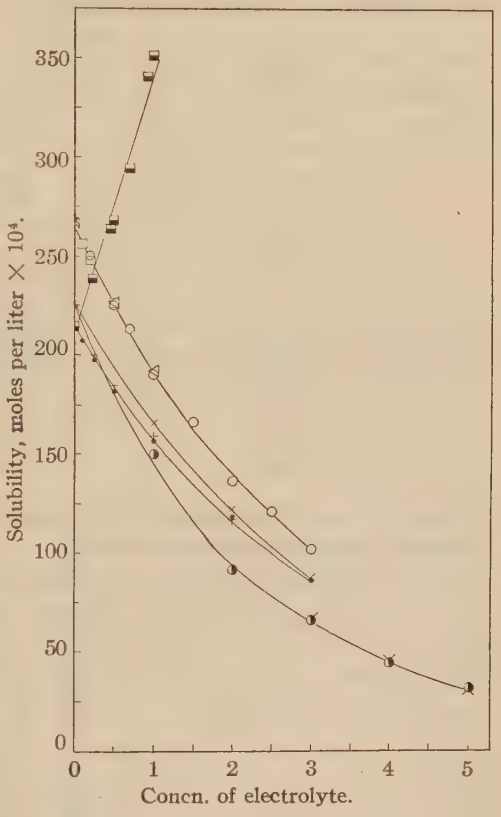
These results and those in the previous paper can be calculated to mole fractions or molalities with an accuracy within that of the measurements by using the densities for potassium chloride solutions as given in the "International Critical Tables."

Figure 1 shows graphically the change of the solubility of molecular benzoic acid with the nature and concentration of the solvent electrolyte. With our values at 25.15° are shown those of Hoffmann and Langbeck,[4] and Freundlich and Seal[5] at 25° in potassium chloride solutions. Their solutions were not buffered and their determinations give only the total solubility of the benzoic acid. We have calculated the ionized part from

[4] Hoffmann and Langbeck, *Z. physik. Chem.*, **51**, 385 (1905).

[5] Freundlich and Seal, *Kolloid-Z.*, **11**, 257 (1912).

our values of the classical dissociation constant and have subtracted that part from their values. As the plot shows, the agreement is good. The values of Berry[6] in potassium chloride and sodium chloride solutions at 20° are shown with those of Güntelberg and Schiödt[7] at the same temperature. Finally the values obtained by Larsson at 18° are shown for potassium chloride and sodium benzoate solutions.[8] Larsson finds a decidedly opposite effect for sodium benzoate, that is to say, the solubility of molecular benzoic acid is increased by the solvent salt, sodium benzoate.[9] The effect of sodium benzoate is noticeable in our buffers but is probably less than 1% for the benzoate ion concentrations used. It does, however, emphasize the dependence of the electrolyte effect upon the individual nature of the solvent salt. For the solvent salts potassium chloride and sodium chloride the solubility of molecular benzoic acid decreases rapidly with increasing salt concentration. The effect is greater for sodium chloride than for potassium chloride.



In KCl: ⊙, K.+ C.; ◁, F. + S.; ⊡, H. + L. at 25°; ×, B. at 20°; +, ●, L. at 18°. In Na Benzoate: ◘, L. at 18°. In NaCl: ◑, B. at 20°; ∨,∧, G. + S. at 20°; ◉ unbuffered + buffered.

Fig. 1.—Solubility of molecular benzoic acid.

In Table II the classical dissociation constant, $K_c = C_{H^+} C_{B^-}/C_{HB}$ has been calculated from our determination of $C_{H^+} C_{B^-}$ by the electrometric and catalytic methods, and

[6] These determinations were carried out by Mr. W. H. Berry with one of us (M. K., Jr.).

[7] Güntelberg and Schiödt, *Z. physik. Chem.*, **135,** 393 (1928).

[8] Larsson, *ibid.*, **148A,** 304 (1930).

[9] Since this thesis was submitted Larsson has reported a number of salts which increase the solubility of benzoic acid. He has also investigated the effect of temperature on the activity coefficient of molecular benzoic acid. Larsson, *ibid.*, **153A,** 309, 466 (1931).

from the solubility of molecular benzoic acid in the solutions at each electrolyte concentration.

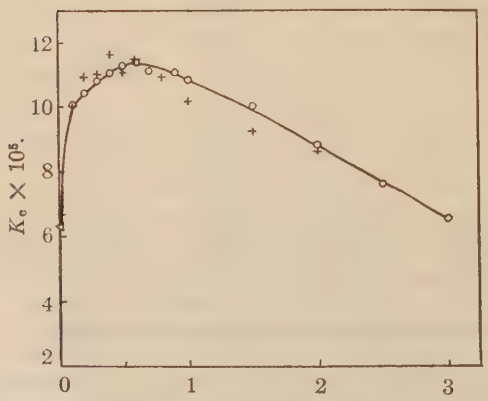
TABLE II

THE DISSOCIATION CONSTANT OF BENZOIC ACID IN POTASSIUM CHLORIDE SOLUTIONS AT 25.15°

KCl + NaB, moles per liter	$C_{H^+} C_{B^-}$ × 10^7, e. m. f.	$C_{H^+} C_{B^-}$ × 10^7, cat.	C_{HB}, moles per liter	K_c × 10^5, cat.	K_c × 10^5, e. m. f.
0.1	25.7	25.8	0.0255	10.12	10.08
.2	26.1	27.4	.0250	10.96	10.43
.3	26.1	26.8	.0241	11.12	10.83
.4	25.8	26.9	.0231	11.64	11.18
.5	25.5	24.9	.0225	11.07	11.32
.6	24.9	25.5	.0219	11.64	11.38
.7	23.7		.0213		11.12
.8		22.5	.0206	10.92	
.9	22.1		.0199		11.10
1.01	20.5	19.3	.0190	10.16	10.79
1.5	16.5	15.3	.0166	9.22	9.94
2.0	12.1	11.8	.0137	8.61	8.84
2.5	9.19		.0121		7.58
3.0	6.65		.0102		6.52

Figure 2 shows the change of the dissociation constant of the acid with increasing electrolyte concentration.

Table III gives the values of the dissociation constant obtained by Berry and by Güntelberg and Schiödt for potassium chloride and sodium chloride solutions.



○, E. m. f.; +, catalytic; ◁, conductivity.

Fig. 2.—Electrolyte effect on the dissociation constant of benzoic acid.

In order to emphasize the fact that the change of dissociation constant with changing electrolyte concentration is different for different acids of the same type in the same solvent salt, we have plotted in Fig. 3 the ratio K_c/K_a for benzoic acid, acetic acid, formic acid and carbonic acid. The values for acetic acid and formic acid are calculated from the papers of Harned and Murphy[10] and Harned and Owen,[11] respectively. The values for the first dissociation constant of carbonic acid are from Güntelberg and Schiödt.[7]

[10] Harned and Murphy, THIS JOURNAL, **53**, 8 (1931).

[11] Harned and Owen, *ibid.*, **52**, 5079 (1930).

TABLE III

COMPARISON OF K_c FOR BENZOIC ACID IN SODIUM AND POTASSIUM CHLORIDE SOLUTIONS

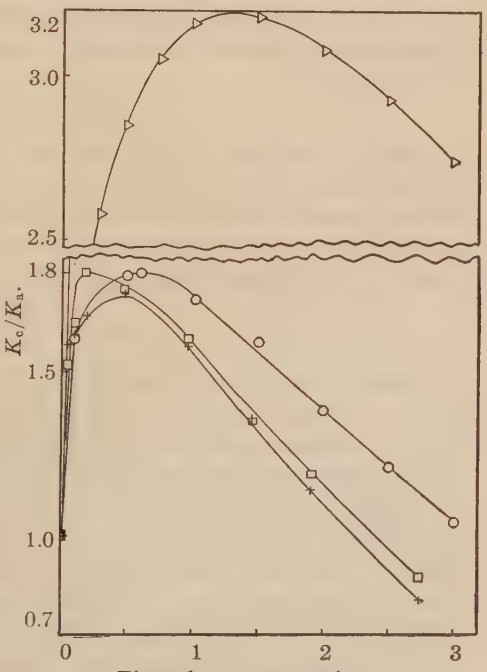
KCl + NaB, moles per liter	$C_{H^+} C_{B^-} \times 10^7$, Berry, 20°	C_{HB} moles per liter, Berry, 20°	$K_c \times 10^5$, Berry, 20°	$K_c \times 10^5$, G. and S., 20°
1.0	16.9	0.0166	10.18	
2.0	9.81	.0123	7.98	
3.0	5.33	.0880	6.06	5.84
NaCl + NaB				
1.0	16.2	.01500	10.80	
2.0	8.61	.00918	9.38	
3.0	4.20	.00656	6.40	6.25
3.0	1.76	.00442	3.98	4.03
5.0	0.717	.00313	2.29	2.46

The curves for formic and acetic acids are similar, while that for carbonic acid is strikingly different, the maximum value of K_c for carbonic acid being over three times K_a. In general the K_c/K_a curve is different for different monobasic acids. These differences are attributed to two causes, the salting out effect on the ions and molecules and the interaction effect which depends on the deformability. Güntelberg and Schiödt[7] have given an interesting discussion of the effect of these factors upon the dissociation constant of a given acid in different solvent salt solutions.

The change of the mean activity coefficient of the ions of benzoic acid with potassium chloride concentration as determined in a previous paper[3] is given by the extended Debye–Hückel equation

$$-\log \sqrt{f_{H^+} f_{B^-}} = \frac{0.5\sqrt{c}}{1 + \kappa b} + \beta c$$

where $\kappa = 0.33 \times 10^8 \sqrt{c}$, b is the apparent average ionic diameter, taken here as 5.15×10^{-8} cm., β is an empirical constant taken



All in KCl: ▷, carbonic acid, G. + S.; ○, benzoic acid; +, acetic acid, H. + M.; □, formic acid, H. + O.

Fig. 3.—K_c/K_a *vs.* electrolyte concentration.

equal to -0.139, and c is the electrolyte concentration in moles per liter. Below we show that

$$\log f_{HB} = 0.138\, c$$

Since

$$K_c = K_a \frac{f_{HB}}{f_{H^+} f_{B^-}}$$

we have

$$\log K_c = \log K_a + \log f_{HB} - \log f_{H^+} f_{B^-}$$

and substituting

$$\log K_c = \log K_a + 0.138\, c + 2\left[\frac{0.5\sqrt{c}}{1 + 1.70\sqrt{c}} + \beta c\right]$$

Taking $K_a = 6.31 \times 10^{-5}$, we have

$$\log K_c = -4.200 + \frac{\sqrt{c}}{1 + 1.70\sqrt{c}} - 0.140\, c$$

an equation which gives our values for K_c for solutions containing from 0.1 mole per liter to 3 moles per liter of potassium chloride within 2%.

Since all the solutions were saturated with benzoic acid, the activity of the molecular benzoic acid remained constant and equal to its solubility in pure water

$$a_{HB} = f_{HB}\, c_{HB}$$

the activity coefficient, f_{HB}, being set equal to one at zero electrolyte concentration. Upon subtracting the ionized part as calculated from conductivity measurements from the solubility of benzoic acid in water, and upon making a small correction for the ion concentration ($\mu = 0.0013$), a value of 0.02650 mole per liter is obtained.[3] Thus

$$f_{HB} = \frac{0.02650}{c_{HB}}$$

The values of the activity coefficient calculated in this way are given in Table IV and for comparison we have included a summary of the results of Berry, Hoffmann and Langbeck, Güntelberg and Schiödt and Larsson.

An inspection of the table shows that for low electrolyte concentration the activity coefficient is practically independent of temperature over the range given.

Some of these values are shown graphically in Fig. 4, where the logarithm of the activity coefficient is plotted against the electrolyte concentration.

An equation of the form $\log f = kc$ expresses the results very well. For our results at 25.15° in potassium chloride solution

$$\frac{\log f}{c} = 0.138$$

For the results of Berry at 20° and of Güntelberg and Schiödt at 25° in sodium chloride solution

$$\frac{\log f}{c} = 0.176$$

TABLE IV

COMPARISON OF VALUES OF f_{HB}

Electrolyte, KCl, moles per liter	Buffers, 25°	Hoffmann and Langbeck, 25°	Freundlich and Seal, 25°	Larsson, buffers, 18°	Larsson unbuff., 18°	G. and S. buff., 20°	Berry, buff., $\frac{0.02265}{C_{HB}}$ 20°
0	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)
0.05		1.02					
.1	1.04	1.04			1.04		
.2	1.06	1.07					
.26				1.08	1.09		
.3	1.10						
.33		1.11					
.4	1.15						
.5	1.18	1.18	1.18	1.18	1.18		
.6	1.21						
.7	1.25						
.9	1.33						
1.01	1.40		1.39	1.37	1.37		1.37
1.5	1.60						
2.0	1.94			1.86	1.81		1.84
2.5	2.19						
3.0	2.61			2.57		2.55	2.58
NaCl							
0				(1.00)	(1.00)	(1.00)	(1.00)
0.25				1.11			
.5				1.23	1.24		
1.0				1.51	1.49		1.51
2.0				2.26	2.25		2.47
3.0				3.38	3.35	3.40	3.46
4.0						5.05	5.14
5.0						7.50	7.25

At 18° Larsson gives the values

$$k = 0.137 \text{ for KCl}$$
$$k = 0.177 \text{ for NaCl}$$

When the concentrations are expressed in moles per 1000 g. of water, and $\log \gamma$ is plotted against m, the points do not lie on a straight line as in Fig. 3. The best line which can be drawn, however, is represented by the equation

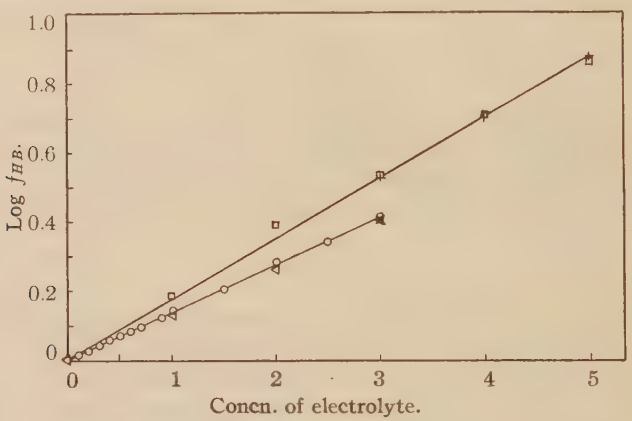
$$\log \gamma = 0.12\, m$$

Using the data on the solubility of benzoic acid available at that time, Randall and Failey[12] gave $k = 0.13$ for potassium chloride and 0.18 for sodium chloride solution.

The activity coefficient of benzoic acid is larger in sodium chloride solution than in potassium chloride solution, that is to say, the solubility is less in sodium chloride than in potassium chloride solution of the same concentration. Since the salting out effect depends on the change in the

[12] Randall and Failey, *Chem. Reviews*, **4**, 291 (1927).

orientation of the water molecules toward the neutral molecule, one would expect the smaller sodium ion to have a greater effect than the larger potassium ion. This is in agreement with the facts and theory as discussed by Debye and McAulay[13] and Scatchard and others.[14] As pointed out by Scatchard, various Hofmeister series have been put forward for the cations and anions. Glasstone and Pound,[15] who studied the electrolyte effect on the solubility of ethyl acetate, give the order $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ and $Cl^- > Br^- > I^-$ for decreasing solubility of ethyl acetate. Linderström-Lang[16] shows the same order for hydroquinone, quinone and succinic acid (uncorrected for the dissociated part).



○, E. m. f., 25°; ◁, Berry, 20°; ×, G. + S., 20°, in KCl; □, Berry, 20°; +, G. + S., 20°, in NaCl.

Fig. 4.—Activity coefficients of molecular benzoic acid in potassium chloride and sodium chloride solutions.

Haesseler[17] finds the same general order for benzoic acid. Haesseler reports the solubility of total benzoic acid and has not corrected in any way for the part present as ions. Larsson demonstrated that the salting out of benzoic acid is, roughly speaking, an additive property of the ions of the solvent salt, *i. e.*

$$\log f = kc = [k_{C^+} + k_{A^-}]c$$

he arbitrarily set k_{K^+} equal to k_{Cl^-}, and calculated salting out constants for all the ions of the solvent salts studied.

In Table V we give some of Larsson's[18] ionic salting out constants and in

[13] Debye and McAulay, *Physik. Z.*, **24**, 185 (1923).
[14] Scatchard, *Chem. Reviews*, **3**, 383 (1927).
[15] Glasstone and Pound, *J. Chem. Soc.*, **127**, 2660 (1925).
[16] Linderström-Lang, *Compt.-rend. trav. lab. Carlsberg*, **15**, 4 (1924).
[17] Haesseler, Dissertation, Columbia University, 1929.
[18] Larsson, *Z. physik. Chem.*, **153**, 299 (1931).

addition the radii of the ions as calculated by Pauling[19] for crystals. While these radii will not necessarily be the same in solution they will probably have the same relative magnitudes.

TABLE V

COMPARISON OF IONIC SIZE WITH SALTING OUT CONSTANT, k

Ion	Radius, Å.	k	Ion	Radius, Å.	k
Li^+	0.60	0.12	Mg^{++}	0.65	0.10
Na^+	0.95	.11	Ca^{++}	0.99	.10
K^+	1.33	.07	Sr^{++}	1.13	.09
Rb^+	1.48	.02	Ba^{++}	1.35	.08
Cs^+	1.69	−.08			
			Cl^-	1.81	0.07
			Br^-	1.95	0.00
			I^-	2.16	−0.02

From Table V it appears that k decreases with increasing ion size. In order to go further with any theoretical discussion, one would have to have information as to the change in dielectric constant and freezing points of these solutions, as pointed out by Debye and McAulay and Scatchard, as well as some knowledge of the deformability of the ions and molecules. Larsson points out that his results are qualitatively in agreement with the available dielectric data. The further study of the solubility of molecular benzoic acid in salt solutions offers a number of interesting possibilities, especially in view of the increase of solubility of benzoic acid in solutions of sodium benzoate ($k = -0.21$) and a number of other salts such as sodium β-naphthalene sulfonate ($k = -0.75$).

Summary

1. The solubility at 25.15° of benzoic acid in potassium chloride solutions has been determined and from determinations of the hydrogen-ion concentrations of these solutions the solubility of molecular benzoic acid has been calculated.

2. From these solubility values and the values of the ion product $C_{H^+}\ C_{B^-}$, the classical dissociation constant of benzoic acid has been calculated at the various electrolyte concentrations from 0.1 to 3.0 moles per liter.

3. A comparison of the change of the dissociation constant with electrolyte concentration has been given for different acids in the same solvent salt.

4. The activity coefficient of molecular benzoic acid in potassium chloride solutions has been evaluated. The results are expressed by the equation $\log f = 0.138c$.

5. A discussion of the relation of ion size to salting out has been given.

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[19] Pauling, THIS JOURNAL, 49, 765 (1927).

[Reprint from the Journal of the American Chemical Society, 54, 2284 (1932).]

[Contribution from the Laboratory of Physical Chemistry of the University of Pennsylvania]

THE CLASSICAL DISSOCIATION CONSTANT OF BROMCRESOL GREEN, CHLORPHENOL RED AND METHYL RED IN POTASSIUM CHLORIDE SOLUTIONS[1]

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A great part of the work in the colorimetric determination of hydrogen-ion concentration has been based on the incorrect assumption that equal color in solutions of equal indicator concentration meant equal hydrogen-ion concentration. That this assumption leads to errors of considerable magnitude has been clearly pointed out by Güntelberg and Schiödt.[2] They show that for the case studied by Szyszkowski[3] the error due to the above assumption amounted to several hundred per cent. Consequently, this error is of the greatest importance and a clear understanding of the factors involved is essential.

An indicator is nothing more than a weak acid, or base, where the acid form, or basic form, or both, is colored due to some structural rearrangement. Thus we can have a buffer system just as with any weak electrolyte

[1] Abstracted from the thesis of Elwyn F. Chase presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1931.

[2] Güntelberg and Schiödt, *Z. physik. Chem.*, **135**, 393 (1928).

[3] Szyszkowski, *ibid.*, **58**, 420 (1907).

and the classical dissociation constant is a good measure of the acid strength. If we consider the acid HI the classical dissociation constant is

$$K_c = \frac{C_{H^+} \cdot C_{I^-}}{C_{HI}} \quad (1)$$

where C_{H^+} really represents $C_{H_3O^+}$. At the half transformation point $C_{HI} = C_{I^-}$ and

$$K_c = C_{H^+} \quad (2)$$

Now it is generally known that K_c changes with change in electrolyte concentration. In the case of monobasic acids these changes depend not only on the electrolyte concentration but also on the particular acid and electrolyte.[4] The magnitude of these changes will also depend on the ion charge types involved but this will not affect the general equations derived below. If we consider two solutions I and II at the half change point or any other degree of transformation, *i. e.*, C_{I^-}/C_{HI} ratio, from equation (2) it follows that

$$\left(\frac{C_{H^+}}{K_c}\right)_I = \left(\frac{C_{H^+}}{K_c}\right)_{II} \quad (3)$$

If I is the known and II is the unknown, then

$$(C_{H^+})_{II} = (C_{H^+})_I \cdot \frac{(K_c)_{II}}{(K_c)_I} \quad (4)$$

an equal color means equal hydrogen-ion concentration when $(K_c)_{II}/(K_c)_I$ is equal to unity. In other words, $(K_c)_{II}/(K_c)_I$ is the term expressing the so-called "salt error" of indicators. The ratio $(K_c)_{II}/(K_c)_I$ may change several fold[4] so that the determination of the classical dissociation constants of indicators is essential to the use of the colorimetric method. The present paper deals with the determination of the classical dissociation constants of bromcresol green, chlorphenol red and methyl red in aqueous potassium chloride solutions.

The method of determining the classical dissociation constant depends upon having solutions of suitable known hydrogen-ion concentration and determining experimentally the ratio of the basic and acid forms of the indicator in such solutions. Substitution of these values in equation (1) gives the dissociation constant directly. This method has been used by Friedenthal[5] and improved upon by Gillespie.[6] For indicators having half-change points around 0.01 molar hydrogen-ion concentration, it is convenient to use solutions of strong acid as standard but it is not practicable to work in glass with large amounts of salt present at concentrations of strong acid much below 1×10^{-3}. Besides, in unbuffered solutions of this sort one must take into account the buffering action of the

[4] For examples see Chase and Kilpatrick, THIS JOURNAL, **53**, 2589 (1931).

[5] Friedenthal, *Z. Elektrochem.*, **10**, 114 (1904); Salm, *Z. physik. Chem.*, **57**, 471 (1906).

[6] Gillespie, THIS JOURNAL, **42**, 742 (1920).

indicator system.[7] In the present study the standards have been the buffer systems of benzoic acid–benzoate, acetic acid–acetate, cacodylic acid–cacodylate and hexahydrobenzoic acid–hexahydrobenzoate. In the first case the hydrogen-ion concentrations were those calculated from the values of the classical dissociation constant of benzoic acid in potassium chloride solutions as given by Chase and Kilpatrick.[4] In the other cases the hydrogen-ion concentrations were determined by means of the quinhydrone electrode under the same assumptions used in the standardization of the benzoic acid–benzoate system.[8]

Experimental Method

As preliminary experiments showed that different samples of indicator gave different values, we attempted to obtain the purest possible samples of the indicators.[9] Two samples of bromcresol green (tetrabromo-*m*-cresolsulfonephthalein) were used. The first was crystallized from acetic acid. The second was also crystallized from glacial acetic acid and analysis showed 44% bromine as against a calculated value of 45.8%. The indicator solutions were prepared by shaking a weighed amount of the indicator acid with a dilute solution of sodium hydroxide containing the calculated amount to form the sodium salt. The solution was then centrifuged and diluted to a convenient concentration. Preliminary experiments[10] with another indicator (bromphenol blue) have shown that in the presence of sodium hydroxide of concentration 3×10^{-3} molar and an indicator concentration of 2×10^{-5} molar the blue color disappears completely in about fourteen days. This change seems to be proportional to the hydroxyl-ion concentration and from a study of the increase in the rate of the reaction with increasing potassium chloride concentration (primary kinetic salt effect) appears to be a reaction between two ions. Since the solutions gave tests for the bromide ion, it seems likely that the bromine is replaced by the hydroxyl ion in the compound. For this reason we avoided using the method recommended by Clark[11] in which the indicators are ground up with 0.01 molar sodium hydroxide solutions. In fact in later work we have been using the following method to carry out the neutralization more quickly and thus avoid an excess of sodium hydroxide. The indicator is dissolved in alcohol, the calculated amount

[7] This has been pointed out by Fawcett and Acree, *Ind. Eng. Chem., Anal. Ed.*, **2**, 78 (1930), and Kolthoff, THIS JOURNAL, **53**, 825 (1931).

[8] Kilpatrick and Chase, *ibid.*, **53**, 1732 (1931).

[9] The bromcresol green and chlorphenol red were specially purified and furnished to us through the kindness of Drs. D. Twiss and W. C. Harden of the Chemical Research Laboratory of Hynson, Westcott and Dunning Co., Baltimore, Md.

[10] Experiments carried out with C. E. Gulezian.

[11] Clark, "The Determination of Hydrogen Ions," 3d ed., Williams and Wilkins Co., Baltimore, Md.

of aqueous sodium hydroxide added, the alcohol evaporated under reduced pressure and the residue taken up in distilled water.

Two samples of chlorphenol red (dichlorophenolsulfonephthalein) were used. The first was purified by repeated solution in sodium carbonate and precipitation by hydrochloric acid. This sample did not dissolve completely in sodium hydroxide. A second sample purified by Harden[12] dissolved completely and immediately in very dilute sodium hydroxide. The second sample gave the following analysis: calcd., sulfur, 7.58; chlorine, 16.76. Found: S, 7.60; Cl, 16.66. A comparison of the dissociation constants of these samples will be given later.

Methyl red (*o*-carboxybenzene-azo-dimethylaniline) was purified by repeated crystallization from toluene. The sample gave a sharp melting point between 176 and 177°.

The stock solutions of the indicators were diluted to a concentration of 5×10^{-4} molar and contained potassium chloride ranging from 0.1 to 3 molar. The colorimeter was of the Gillespie type and is described by Clark.[13] In all cases the acid form and the basic form were obtained by adding the calculated amount of hydrochloric acid or sodium hydroxide for over 99% conversion.

TABLE I

THE CLASSICAL DISSOCIATION CONSTANT OF BROMCRESOL GREEN IN POTASSIUM CHLORIDE SOLUTIONS

Buffers: benzoic acid–benzoate, acetic acid–acetate, hexahydrobenzoic acid–hexahydrobenzoate. Temp., about 25°; indicator, about 5×10^{-5} mole per liter

Electrolyte KCl + NaX moles per liter	Average $K_c \times 10^5$	Number of detns.	a. d., %
0.1000	3.07 (2.33*k*)	6	3.5
0.5000	4.03 (3.13*k*)	5	2.6
1.000	3.61	9	6.4
1.500	3.46	6	3.6
2.000	2.93	5	5.8
2.500	2.55	6	4.9
3.000	2.38	3	3.8

X, anion of acid used in buffer. *k*, values chosen by Kolthoff.

Table I gives the results with bromcresol green. Column I gives the electrolyte concentration, which is largely potassium chloride. Column II gives the average value of K_c with a value calculated from the values of Kolthoff, given in his recent survey of indicator constants.[14] Kolthoff gives the values in terms of pK_1 and states that the accuracy is supposed to be within 0.05 of a logarithmic unit (12% in K_1). K_1 does not represent the classical dissociation constant but a dissociation constant defined by the equation

[12] Harden, THIS JOURNAL, **52**, 4611 (1930).

[13] Clark, Ref. 11, p. 169.

[14] Kolthoff, *J. Phys. Chem.*, **34**, 1466 (1930).

$$pK_1 = P_H - \log \frac{C_B}{C_A} \quad (5)$$

where P_H is the Sörensen P_H. The classical dissociation constant is related to this constant (K_1) by the equation

$$pK_c = pK_1 - pf_H + 0.04 \quad (6)$$

$-\log f_H$ was evaluated, with sufficient accuracy, from the empirical equations of Bjerrum and Unmack[15] and K_c was calculated from the values of Kolthoff for K_1. Our observed values, which are higher than those given by Kolthoff, were obtained with two different indicator samples and three different buffer systems.

TABLE II

THE CLASSICAL DISSOCIATION CONSTANT OF CHLORPHENOL RED IN POTASSIUM CHLORIDE SOLUTIONS

Buffers: Cacodylic acid–cacodylate. Temp., about 22°. Indicator, about 2.5×10^{-5} moles per liter

Electrolyte, KCl + NaX, moles per liter	Average $K_c \times 10^7$	Number of detns.	a. d., %
0.1000	11.0 (10.7k)	3	6.7
0.5000	13.4 (13.5k)	3	5.4
1.000	16.2	2	1.9
1.500	13.1	2	2.1
2.000	13.2	2	2.3
2.500	9.45	2	4.9
3.000	7.90	2	10.0

X, cacodylate. k, values chosen by Kolthoff at 20°.

Table II gives the results for chlorphenol red in cacodylic acid–cacodylate buffers in potassium chloride solutions. The results with the first sample

TABLE III

THE CLASSICAL DISSOCIATION CONSTANT OF METHYL RED IN POTASSIUM CHLORIDE SOLUTIONS

Buffers: Acetic acid–acetate. Temp., about 22°. Indicator, about 1.3×10^{-5} moles per liter

Electrolyte, KCl + NaX, moles per liter	Average $K_c \times 10^6$	Number of detns.	a. d., %
0.1000	10.4 (10.7k)	5	2.2
0.5000	9.21 (10.7k)	3	2.9
1.000	7.75	2	5.8
1.500	6.25	2	7.8
2.000	5.33	2	2.6
2.500	3.61	3	3.8
3.000	2.90	2	12.0

X, acetate. k, value chosen by Kolthoff at 20° for electrolyte concentrations from zero to 0.5 mole per liter ($10.7 \times 10^{-6} \pm 12\%$).

[15] Bjerrum and Unmack, *Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.*, **9**, 1 (1929)

of indicator were much lower and are not included. For example, the dissociation constant for the first sample at one molar potassium chloride concentration was 7.7×10^{-7} as compared with 16.2×10^{-7} for the second sample.

Table III gives the results for methyl red. Methyl red is of particular interest in that it is an indicator of the ampho-ion type. Considering the structure

$$(CH_3)_2N—C_6H_4—N_2—C_6H_4—COOH$$

the molecule contains a basic group as well as an acid group. The amino group will tend to pick up protons to form the ampho-ion

$$(CH_3)_2NH^+—C_6H_4—N_2—C_6H_4—COO^-$$

In acid solution we have the form

$$(CH_3)_2NH^+—C_6H_4—N_2—C_6H_4—COOH$$

and in basic solution

$$(CH_3)_2N—C_6H_4—N_2—C_6H_4—COO^-$$

The dissociation constant is related to the dissociation constant at zero ion concentration by the equation

$$K_c = K_{c_0} \frac{f_{HI^\pm}}{f_{H^+} f_{I^-}}$$

Now Bjerrum[16] has shown that in dilute solution an ampho-ion behaves like a neutral molecule and in more concentrated solution like two ions. Consequently in very dilute solution

$$K_c = K_{c_0} \frac{1}{f_1^2}$$

Thus in dilute solution an exponential salt effect would be expected. In more concentrated solution the activity factor would be such

$$K_c = K_{c_0} \frac{f_1^2}{f_1^2}$$

that a linear salt effect would be expected. The curve for methyl red in Figure 1 shows this effect. The exponential effect below 0.1 molar was not investigated due to the fact that the assumptions involved in the electrometric method for determining the hydrogen-ion concentration are not valid below 0.1 molar. Güntelberg and Schiödt[2] do indicate the exponential part in the case of methyl orange. In this connection we cannot agree with the statement of Kolthoff[14] that the salt error of methyl orange is extremely small between 0.0 and 0.5μ. If we express the salt error as K_c/K_{c_0} and use the results of Güntelberg and Schiödt, the error is 32% between $\mu = 0.0$ and $\mu = 0.1$.

The curves for bromcresol green and chlorphenol red show that K_c increases with increasing electrolyte concentration, passes through a maximum and then decreases.

[16] Bjerrum, *Z. physik. Chem.*, **104**, 147 (1923).

The Colorimetric Method.—In using the colorimetric method to determine the hydrogen-ion concentration of an unknown solution, one may simply reverse the method employed here in determining the dissociation constant of the indicator, that is, the ratio of the acid form to the basic form of the indicator is determined and the concentration of the hydrogen ion calculated from the equation

$$C_{H^+} = K_c \frac{C_A}{C_B}$$

where K_c is the correct value of the dissociation constant of the indicator for the particular electrolyte, electrolyte concentration and medium used.

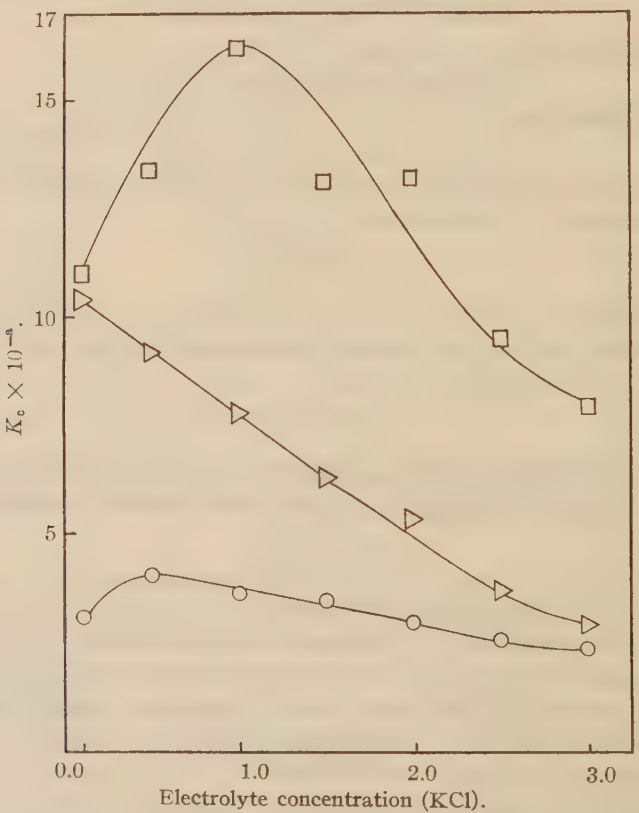

Fig. 1.—K_c for bromcresol green, chlorphenol red and methyl red in potassium chloride solutions: ○, B.C.G. (scale $\times 10^{-6}$); □, C.P.R.(scale $\times 10^{-7}$); ▷, M.R. (scale $\times 10^{-6}$).

More often the unknown is matched with a standard and the hydrogen-ion concentration calculated by equation (4). In other words the ratio of the values of the dissociation constant of the indicator in the unknown and in the standard must be known. At present these standards are

usually given in Sörensen pH or $p\alpha H$ units, because the electrometric method is considered the standard. The resulting confusion can be avoided in dealing with aqueous solutions by calibrating a suitable set of standard solutions in terms of the hydrogen-ion concentration. A convenient standard is a buffer system: 0.01 molar in a suitable monobasic acid, 0.01 molar in the salt of the same acid and 0.09 molar in potassium chloride. The hydrogen-ion concentration of such buffers can be determined electrometrically, catalytically or colorimetrically, the measurements being referred directly to a solution of strong acid. In order to standardize colorimetrically one would determine the dissociation constants of a less sensitive indicator and then use that indicator to standardize a buffer system of an acid of slightly lower dissociation constant than the indicator. By extending this process to weaker acids the range could be extended.

Table IV gives the values of $K_c/K_{c(0.1)}$ for the three indicators and Fig. 2 presents these ratios graphically. Figure 2 also includes the $K_c/K_{c(0.1)}$ values for the acids used in determining the dissociation constant of the indicators.

TABLE IV

THE $K_c/K_{c(0.1)}$ RATIOS IN POTASSIUM CHLORIDE SOLUTIONS

Electrolyte, KCl + NaX, moles per liter	B. C. G.	C. P. R.	M. R.
0.1	1.00	1.00	1.00
0.5	1.31	1.22	0.89
1.0	1.18	1.48	.75
1.5	1.13	1.20	.61
2.0	0.95	1.20	.51
2.5	.83	0.86	.35
3.0	.78	.72	.28

In order to determine the hydrogen-ion concentration the unknown is matched with the standard at equal indicator concentration and the hydrogen-ion concentration of the standard multiplied by the appropriate value from Table IV. If another concentration of electrolyte is used as standard then we simply multiply the above values by the $K_{c(0.1)}/K_{c(\text{standard})}$ ratio. If another electrolyte than potassium chloride is present in the unknown it would be necessary to know the dissociation constant of the indicator in a solution of that electrolyte at the concentration in question. The magnitude of these differences can be seen from a comparison of the dissociation constants of acetic acid in potassium chloride and sodium chloride solutions as taken from Larsson and Adell.[17] The differences up to 0.2 molar are within the experimental error and then increase so that at 3 molar the difference is 12%. Harned and Murphy[18]

[17] Larsson and Adell, *Z. physik. Chem.*, [A] **156**, 352 (1931).

[18] Harned and Murphy, THIS JOURNAL, **52**, 5079 (1930).

report differences at 0.1 molar concentration. For bromphenol blue Güntelberg and Schiödt give K_c in 3 molar potassium chloride as 11.0×10^{-5} and in 3 molar sodium chloride as 9.4×10^{-5}. For higher valence types the differences would be greater and for accurate work it would be necessary to know the dissociation constant in the medium used. It might be emphasized here that no method of expressing the salt error will avoid these second order effects. The same statement should be made in regard to the effect of non-electrolytes and this part of the solute effect may be more important than is generally realized. In any case it is believed that the above method of expressing salt error in indicator work calls attention to the magnitude of the effect and gives a simple method of correcting for it.

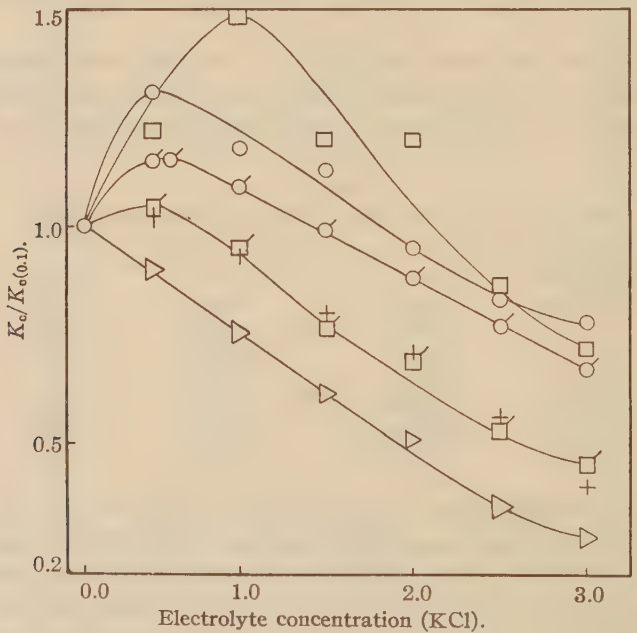

Fig. 2.—$K_c/K_{c(0.1)}$ for B. C. G., C. P. R., M. R., benzoic acid, acetic acid and cacodylic acid in potassium chloride solutions: ○, B. C. G.; □, C. P. R.; ▷, M. R.; ○-, benzoic acid; □-, cacodylic acid; +, acetic acid.

Summary

The classical dissociation constants of bromcresol green, chlorphenol red and methyl red in potassium chloride solutions have been determined.

A simple method of expressing salt errors in colorimetric determinations of hydrogen-ion concentration has been given.

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